

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Preparation of Tertiary-Butyl-Hydroquinone

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343 State Street, Rochester, New York, United States of America (Assignees of DEWALT SECRIST YOUNG and GEORGE FARRIS RODGERS), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing mono - tertiary - butyl - hydroquinone.

We have found that if it is attempted to introduce one tertiary butyl group into hydroquinone by a known process for butylating *p*-methoxyphenol which comprises reacting on the latter with tert.-butyl alcohol or isobutylene in the presence of phosphoric acid catalyst and a solvent for the alkylated phenol such as pentone, hexane, heptane or straight run naphthas from which alkylatable aromatic compounds have been removed, only a very small proportion of the hydroquinone is converted to the desired product, much of the di-tertiary butyl derivative being formed, as is illustrated by the following experiment:—

EXPERIMENT

110 grams of hydroquinone, 400 ccs. of 85% phosphoric acid, and 300 mls. of heptane were mixed, heated to reflux at 88° C., and 74 grams of tert.-butyl alcohol was added over a 30-minute period. When the addition was complete, the hot mixture consisted of a muddy acid layer and a white tarry solvent layer which could not be separated by decantation or filtration. The mixture was therefore diluted with three volumes of water and cooled to 25° C., causing the slushy heptane layer to further harden enough to be filtered from the aqueous solution. The

heptane mixture was then suspended in hot water and the solvent removed by steam distillation. The hot aqueous suspension was filtered to remove 80.4 grams of di-tertiary butylhydroquinone and the filtrate was cooled to bring about crystallization of the tert.-butyl-hydroquinone. The tert.-butyl-hydroquinone was filtered from two litres of water and the weight isolated was 20.5 grams which had a melting point of 125–28° C. The percent conversion based on the hydroquinone was 12.2 percent.

Another known process for preparing alkylated phenols comprises reacting with a tertiary olefine, such as isobutylene, on a phenol, such as phenol itself or resorcinol in the presence of a catalytic amount of mineral acid condensing agent such as sulphuric acid or phosphoric acid and an inert solvent, the mole ratio of phenol to acid being for example about 10:1 or higher and the solvent a saturated hydrocarbon such as methyl cyclohexane or petroleum benzene.

According to the present invention there is provided a process for preparing tert.-butyl-hydroquinone which comprises reacting hydroquinone with isobutylene or tert.-butyl alcohol in the presence of an aromatic hydrocarbon containing from 6 to 8 carbon atoms and phosphoric acid at an elevated temperature with agitation. Preferably, the amount of phosphoric acid employed is from about 1 to 6 times the weight of hydroquinone used.

The process of the present invention has the advantages that a high yield of mono-butylated hydroquinone is obtained and the quantity of di-butylated hydroquinone produced is maintained at a minimum.

In the process for the preparation of tert.-butyl-hydroquinone in accordance with the present invention it is a newly discovered and surprising fact that the mono-alkylated derivative first formed is

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immediately and to a surprisingly high degree removed from the hydroquinone-catalyst phase into solution in the aromatic hydrocarbon and is thereby substantially protected from further alkylation. After the reaction is complete, the desired mono-alkylated product can be recovered from the aromatic liquid hydrocarbon by any procedure obvious to those skilled in the art such as by crystallization and filtration. The aromatic liquid can be employed to continuously extract the mono-alkylated product from the reaction mixture as the reaction is in progress.

One of the most important features of the process of the invention is the employment of the aromatic non-miscible liquid hydrocarbon. The use of such a solvent as toluene or xylene is preferred although other aromatic hydrocarbons of the benzene series containing from 6 to 8 carbon atoms can be employed for use in such a process. The amount of aromatic hydrocarbon employed is preferably from about 1 to 2 times the combined weight of hydroquinone and isobutylene or tert-butyl-alcohol.

In the process of the present invention the quantities of the various materials employed can be varied within wide limits. Approximately equimolecular proportions of hydroquinone and tertiary butyl alcohol are employed to obtain the most advantageous results. However, higher and lower proportions within the vicinity of a ratio of 1:1 can be employed. It is advantageous to maintain the molar ratio of hydroquinone to tert-butyl alcohol are employed to obtain the most advantageous results. However, higher and lower proportions within the vicinity of a ratio of 1:1 can be employed. It is advantageous to maintain the molar ratio of hydroquinone to tert-butyl alcohol at a value greater than unity; however, ratios of from about 0.962 to about 1.015 are illustrated by the examples below and a wider variation than this can also be employed. The catalyst employed in accordance with the present invention is phosphoric acid. 85% phosphoric acid is employed in the various examples given below; however, equivalent quantities of other strengths or concentrations of phosphoric acid can also be employed. Substantial proportions of phosphoric acid as compared with the reactants present in the reaction phase are preferably employed, as illustrated in the following examples.

The elevated temperature employed in accordance with the process of the present invention is most advantageously that at which reflux conditions exist.

With proper stirring, temperatures which are higher or lower than that provided by reflux can also be employed. Temperatures of from about 65° to about 110° C. can be advantageously employed. The xylene employed has a boiling point of about 142° C.; the boiling point of toluene is about 110° C. In regard to the temperature employed, a limiting factor is the tendency for isobutylene to escape from the reaction mixture at temperatures substantially higher than 100° C., although a pressure vessel can be employed to avoid this effect. The period required for the reaction can be varied within wide limits; however, there seems to be no reason to prolong the reaction duration beyond several hours.

The water which is formed when tert-butyl alcohol is used as in Examples 1 and 3 below, dilutes the reaction mixture but can be readily removed by azeotropic distillation thereof.

The following Examples 1 to 5 illustrate but do not limit the process of the present invention for preparing tert-butyl-hydroquinone.

EXAMPLE 1

(TOLUENE SOLVENT)

300 cc of toluene, 110 grams of hydroquinone, and 400 cc of 85% phosphoric acid were mixed, heated to 92° C. and 74 grams of tert-butyl alcohol was introduced over a 30-minute period. When the addition was complete, the hot reaction mixture was a two-phase system consisting of a toluene solution and an aqueous phosphoric acid solution. No solid material was present. The hot toluene layer was separated and subjected to steam distillation to remove the aromatic hydrocarbon solvent, leaving behind an aqueous suspension which was filtered hot so as to isolate 37.8 grams of ditert-butyl-hydroquinone. The filtrate was cooled to bring about crystallization of tert-butyl-hydroquinone which was isolated by filtration from 2 litres of water. The weight of tert-butyl-hydroquinone isolated was 49.5 grams which had a melting point of 127–129° C. The percent conversion based on the hydroquinone employed was 29.8 percent.

EXAMPLE 2

(XYLENE SOLVENT)

147 grams of hydroquinone, 250 grams of 85% phosphoric acid and 500 cc of xylene were mixed in a three neck flask provided with thermometer, agitator and reflux condenser. The temperature was increased to 105° with good agitation and 55 grams of isobutylene was introduced over a one-hour period. Next, the supernatant xylene layer was drawn off, and the lower phosphoric acid layer was pre-

The percent conversions given above are based on the quantity of hydroquinone employed in the reaction and demonstrate the high conversion to tert-butyl-hydroquinone which can be obtained by the processes of the present invention. In the seven batches which were run in the above example, the original 1200 grams of phosphoric acid was employed throughout and the original 8000 ml of toluene was supplemented by the addition of only 2300 ml during the course of the succeeding batches.

In addition to the successive batch procedure illustrated in Example 4, a continuous process can be even more advantageously employed for preparing tert-butyl-hydroquinone which comprises (1) admixing approximately equal volumes of phosphoric acid (calculated as 85% phosphoric acid) and an aromatic hydrocarbon containing from 6 to 8 carbon atoms, (2) maintaining this admixture at its boiling point and maintaining the lower portion of this admixture under good agitation while continuously introducing into this admixture approximately equimolecular proportions of hydroquinone and tert-butyl alcohol together with sufficient additional aromatic hydrocarbon to replace that removed as indicated in (3) and (4) as hereinbelow defined, (3) continuously removing water substantially concurrently as it is formed by distilling off an azeotrope of water and aromatic hydrocarbon, (4) continuously removing from the upper part of the liquid reaction mixture a minor portion thereof which comprises a solution of tert-butyl-hydroquinone dissolved in the aromatic hydrocarbon, and (5) separating the tert-butyl-hydroquinone in from this solution.

Materials charged:—

	Hydroquinone	-	-	-	9845 grams
	Tert.-butyl alcohol	-	-	-	6882 grams
	Toluene	-	-	-	13010 grams
90	85% phosphoric acid	-	-	-	745 grams

Products recovered:—

	Hydroquinone	-	-	-	1578 grams
	Tert.-butyl-hydroquinone	-	-	-	9245 grams (62.2% conversion)
	Di-tert.-butyl-hydroquinone	-	-	-	2321 grams (11.7% conversion)

In the above example, the percent yield of tert-butyl-hydroquinone based on the amount of hydroquinone consumed was 74 percent. About 4½% of 85% phosphoric acid was employed based on the total weight of hydroquinone and tert-butyl alcohol employed as starting

EXAMPLE 5 (CONTINUOUS PROCESS)

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Hydroquinone was alkylated with tert-butyl alcohol in a continuous process, the alkylated products being subsequently separated and purified batch-wise. The alkylation was carried out by feeding hydroquinone, tert-butyl alcohol and toluene into the bottom of a cylindrical reactor containing about half its volume of 85% phosphoric acid as the lower layer and the other half filled with toluene as an upper layer. The mixture was well stirred at the bottom but kept relatively quiet at the top to allow good separation of the layers and permit continuous removal of the toluene solution of the product through a side tube at the top of the reactor. The water formed during the reaction was removed continuously by azeotropic distillation. The toluene solution of the product was taken off from the top of the reaction mixture and led into a steam still where the toluene solvent was distilled and returned to a toluene feed tank from which the toluene being withdrawn from the reaction mixture was replaced. When sufficient product had accumulated in the steam still to form a batch, the toluene product being withdrawn was switched to another receiver, and the purification of the product continued batch-wise. The di-tert-butyl-hydroquinone was filtered from the hot toluene-free aqueous slurry and the filtrate cooled to 50° C. The tert-butyl-hydroquinone which crystallized was filtered off, and the mother liquor returned to the steam still for reuse. The results obtained in a 72-hour run with this process are summarized as follows:—

materials in the above example.

Tert-butyl-hydroquinone is an effective agent for the stabilization of various animal and vegetable oils and fats against deterioration. Its potency in this regard is much greater than that of 2,5-di-tert-butyl-hydroquinone.

served for use in the following run. The xylene layer on cooling deposited a white crystalline solid which weighed 154 grams. This material consisted of tert.-butyl-hydroquinone mixed with small amounts of hydroquinone and 2,5-ditert.-butyl-hydroquinone. The crude product was easily purified by recrystallization from hot water to yield pure tert.-butyl-hydroquinone M.P.=127–128° C.

EXAMPLE 3 (XYLENE SOLVENT)

110 grams of hydroquinone, 400 cc of 85% phosphoric acid and 400 cc of xylene were mixed in a three neck flask provided with a thermometer, agitator and reflux condenser. The temperature was raised to 105° C. with good agitation and 73 grams of tert.-butyl-alcohol was introduced with good agitation over a 1-hour period. Next, the supernatant xylene layer was drawn off, and the lower phosphoric acid layer was preserved for use in a subsequent run. The xylene layer on cooling deposited a white crystalline solid which weighed 133 grams. This crude material was substantially tert.-butyl-hydroquinone having a melting point of 127–128° C.

In addition to the procedure illustrated by Examples 1, 2 and 3, a successive batch process can be advantageously employed for preparing tert.-butyl-hydroquinone which comprises (1) admixing under reflux conditions about one mole proportion of hydroquinone, from about 1 to about 5 times the same weight of phosphoric acid and from about 1 to about 2 times the same weight of an aromatic hydrocarbon containing from 6 to 8 carbon atoms, (2) maintaining this admixture at its boiling point under good agitation and gradually introducing into this admixture about one mole proportion of tert.-butyl alcohol while substantially concurrently removing water by azeotropic distillation, (3) thereafter separating while hot the layer containing the principal part of the aromatic hydrocarbon from the layer containing the phosphoric acid and (4) then cooling this layer whereby a product consisting

primarily of tert.-butyl-hydroquinone separates as crystals.

EXAMPLE 4

(SUCCESSIVE BATCH PROCESS)

In this example a series of seven batches was run using the same phosphoric acid and the same toluene throughout. The procedure for the first batch of the series was as follows:—

Batch No. 1:—

242 grams of hydroquinone, 1200 grams of 85% phosphoric acid and 8000 ml of toluene were mixed in a round-bottomed flask and heated to reflux with stirring. 444 grams of tert.-butyl alcohol was added at the rate of 148 grams every 45 minutes; during each such 45-minute period, 36 ml of water was removed azeotropically. Additional quantities of 242 grams of hydroquinone were added at the end of 45 and of 90 minutes, making a total quantity of 726 grams of hydroquinone employed. The addition of the tert.-butyl alcohol was complete in 135 minutes, after which the hot toluene layer was immediately withdrawn and cooled to 15° C. The solid product which formed was removed by filtration and the toluene filtrate returned to the reaction flask for the next run. The solid product was then treated with boiling water and filtered hot to remove the di-tert.-butyl-hydroquinone. The filtrate was cooled to 25° C. to cause the crystallization of the tert.-butyl-hydroquinone. The product was filtered off and the mother liquor was saved for the purification of the next batch.

Batches 2 to 7:—

The second through to the seventh batch were run using the same phosphoric acid and the same toluene as in the first batch. The procedure for each of these batches was the same as for the first batch except that only 660 grams of hydroquinone was employed in each by initially admixing 220 grams of hydroquinone and adding the remainder thereof in two equal portions of 220 grams at the end of 45 minutes and 90 minutes. Otherwise the procedure of the first batch was repeated identically.

RESULTS

Materials charged:—

Hydroquinone	-	-	4686 grams (42.6 mols)
Tert.-butyl alcohol	-	-	3108 grams (42.0 mols)
Toluene	-	-	10300 ml
85% phosphoric acid	-	-	1200 grams

Products recovered:—

Tert.-butyl-hydroquinone	-	4171 grams (59.0%)
Di-tert.-butyl-hydroquinone	-	1222 grams (12.9%)

Tert.-butyl-hydroquinone is useful for the preparation of mixtures of 2- and 3-tert.-butyl-4-methoxyphenol, known as BHA, which mixtures have value as food antioxidants.

Tert.-butyl-hydroquinone is also useful as an intermediate in the preparation of other compounds, such as its dialkyl ethers which are valuable as ingredients in perfumes and have other uses as odorants.

What we claim is:—

1. A process for preparing tert.-butyl-hydroquinone which comprises reacting hydroquinone with isobutylene or tert.-butyl alcohol in the presence of an aromatic hydrocarbon containing from 6 to 8 carbon atoms and phosphoric acid at an elevated temperature with agitation.

2. A process according to Claim 1 in which the amount of phosphoric acid is from about 1 to about 6 times the weight of hydroquinone employed.

3. A process according to any of the preceding claims wherein approximately equimolecular proportions of the hydroquinone and isobutylene or tert.-butyl alcohol are employed.

4. A process according to any of the preceding claims wherein the water formed when tert.-butyl alcohol is used is substantially removed by azeotropic distillation as it forms.

5. A process according to any of the preceding claims wherein the isobutylene or tert.-butyl alcohol is gradually added to a mixture of the hydroquinone, phosphoric acid and aromatic hydrocarbon.

6. A process according to any of the preceding claims which comprises (1) admixing under reflux conditions about one mole proportion of hydroquinone, from about 1 to about 5 times the same weight of phosphoric acid and from about 1 to about 2 times the same weight of an

aromatic hydrocarbon containing from 6 to 8 carbon atoms, and (2) maintaining this admixture at its boiling point under good agitation and gradually introducing into this mixture about 1 mole proportion of tert.-butyl alcohol while substantially concurrently removing water by azeotropic distillation, (3) thereafter separating while hot the layer containing the principal part of the aromatic hydrocarbon from the layer containing the phosphoric acid and (4) then cooling this layer whereby tert.-butyl-hydroquinone separates as crystals.

7. A process according to any of Claims

1 to 5 which comprises, (1) admixing approximately equal volumes of phosphoric acid (calculated as 85% phosphoric acid) and an aromatic hydrocarbon containing from 6 to 8 carbon atoms, (2) maintaining this admixture at its boiling point and maintaining the lower portion thereof under good agitation while continuously introducing therein approximately equimolecular proportions of hydroquinone and tert.-butyl alcohol together with sufficient additional aromatic hydrocarbon to replace that removed as indicated in (3) and (4) as hereinbelow defined, (3) continuously removing water substantially concurrently as it is formed by distilling off an azeotrope of water and aromatic hydrocarbon, (4) continuously removing from the upper part of the liquid reaction mixture a minor portion thereof which comprises a solution of tert.-butyl-hydroquinone dissolved in the aromatic hydrocarbon and (5) separating the tert.-butyl-hydroquinone from this solution.

8. A process according to Claim 6 or 7 in which the aromatic hydrocarbon is recycled.

9. A process according to any of the preceding claims wherein the elevated temperature is from about 65° C. to about 110° C.

10. A process according to any of Claims 1 to 9 wherein reflux conditions are maintained.

11. A process according to any of the preceding claims wherein the weight of aromatic hydrocarbon employed is from about 1 to about 2 times the combined weight of the hydroquinone and isobutylene or tert.-butyl alcohol.

12. A process according to any of the preceding claims wherein the aromatic hydrocarbon is toluene.

13. A process according to any of Claims 1 to 11 wherein the aromatic hydrocarbon is xylene.

14. A process for preparing tert.-butyl-hydroquinone substantially as herein described.

15. Tert.-butyl-hydroquinone whenever prepared by a process according to any of Claims 1 to 14.

16. Compositions comprising a vegetable oil or fat and tert.-butyl-hydroquinone as claimed in Claim 15.

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